T. L. BEWICK.

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PLATINUM THERMOMETERS
FOR LOW TEMPERATURE
MEASUREMENTS.

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BY

THOMAS LYMAN BEWICK

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Outline.

Historical.

Until the last decade platinum thermometry was a term almost without a meaning to the world at large. With the exception of a very few scientists whose attentions had been directed to this subject while in search of some more accurate and convenient method of measuring temperature, few knew anything of it.

The measurement of temperature by means of the variation of resistance of a wire was first seriously proposed by Siemens who submitted for trial and exposition, some platinum resistance pyrometers to a committee of the British Association for the Advancement of Science.* These instruments however, were found unfavorable and faulty in many respects, some of which were then thought unsurmountable.

Prof. H. L. Callendar, an English scientist, was the next to take up this work and to him must be accredited the major part of the success and great perfection to which platinum thermometry has been brought. Prof. Callendar

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* See British Assoc. Report 1874.

succeeded in showing the constancy of the electric properties of platinum, if pure and properly annealed, thus removing one of the greatest points of weakness in the work presented by Siemens. Since this introduction by Callendar much varied and extensive work has been done by Callendar and Griffiths, but other investigators as Heycock & Neville, Dewar & Flemming, Cailletet & Colardeau, and Waidner & Mallory have all brought additional testimony and made valuable accessions to the progress of pyrometry.

Resistance thermometry has not been dependent upon platinum alone but other substances have been used with some success, such as,- manganin, gold, silver, and alloys of platinum and silver or platinum and rubidium. In fact, most of the metals have been more or less experimented with. None however, have as yet supplanted platinum as the best under all conditions. Its choice as the standard metal is the outcome of a very wide and general agreement among all experimentors who have attacked the problem. Iridium though less fusible than platinum is too rare a substance and is hard to work. Similar objections apply to the other metals and alloys are rejected because of the small change of resistance with temperature and the inability to secure a uniform mixture.

In platinum resistance thermometry, a coil of wire is introduced into the space or substance whose temperature

is to be ascertained and the electrical resistance of this coil is measured. Such a coil properly protected and mounted, constitutes a platinum resistance thermometer and the extensive researches of the above named men who have worked at very high, very low, and at ordinary temperatures, establishes beyond a doubt the remarkable accuracy and constancy of this instrument over a very wide range of temperature.

In all work in thermometry the fixing of a scale which can be readily interpolated is an important feature. A platinum temperature scale is one so constructed that a rise of one degree on that scale at any temperature would cause the electrical resistance of a platinum wire to increase by 1/100 of the difference between its resistance at 100°C and 0°C. Assuming that a change in temperature is proportional to the change in resistance a temperature scale can be determined upon in much the same way as we fix the scale of mercury thermometers where change of temperature is assumed proportional to the expansion. The difference in the resistances between two fixed temperatures may be divided into as many equal parts as is desired. But for convenience, a close relationship between the platinum thermometer scale and the mercury thermometer scale should be aimed at.

If R_o =the resistance of the wire at 0°Centigrade, R_{100}

the resistance at 100°C, and R, the resistance at some other fixed point, then a scale can be determined upon, represented by the formula,-

$$pt = \frac{Rt - R_o}{R_{100} - R_o} \times 100,$$

Where pt is the platinum temperature, a name applied to the temperature as above determined. The resistances at the different temperatures on the platinum scale have been shown by Callendar to follow almost exactly, the curve of the parabola, so that in the calibration of any platinum thermometer it is only necessary to determine the resistance at three different points, from which the curve can be found by applying the above formula. In order to change from temperatures on the platinum scale to those on the air scale it is necessary to determine the relation between pt and t. It was found by Callendar and others in the comparisons of platinum and air thermometers that over a wide range of temperature, from 0°C. to 600°C each was well represented by the equation $t - pt = \delta\left[(t/100)^2 - t/100\right]$, where δ is a constant depending upon the chemical composition of the wire.

Theoretically such a thermometer could be made to cover any range of temperature but practically it is more desirable to construct a series of thermometers. For low temperature instruments can be made with a larger fundamental

unit than those constructed for high temperature, which would minimize the risk of error from ~~which~~ variable contacts without incurring trouble from imperfect insulation. Were it possible at all times to secure platinum wire of exactly the same chemical purity we might at once establish a standard platinum scale which could be used for purposes of reference independently of any assumptions as to its relation to the air scale. This, of course is impossible, for different lengths of wire taken from the same sample are often found very different, chemically. The very fact that δ has been found to vary a considerable per cent for different specimens of wire, is perhaps one of the most objectionable and most often criticized features of platinum thermometry.

The method of determining the resistance at any temperature is that of the simple Wheatstone bridge in which the resistances in two of the arms are made equal while the resistance of the thermometer and its leads are balanced against the variable resistance of the box and the compensating leads.

Experimental.

The special problem laid out for this work was the construction and calibration of a dozen or more platinum thermometers which were to be used by Mr. E. S. Burnett, in his research work, on the extension of the Joule-Thompson plug experiment* In the construction of the thermometers several conditions had to be satisfied. Some of these were, that they might be readily and quickly manipulated when taking readings; that they respond quickly to any change in temperature; that it might be possible to remove one of them when so desired, and in case of breakage, without displacing any of the other apparatus connected with it. In order to calibrate these thermometers to any degree of accuracy it was necessary to secure a suitable resistance box and have it standardized.

The only bridge at hand was a student's platinum thermometer bridge which was patterned after the students bridge constructed by the Cambridge Scientific Instrument Co. This, it was thought, would hardly be of sufficient

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*See Thesis by E. S. Burnett 1905.

accuracy to allow of its usage, so through the kindness of the University of Chicago, a box was obtained which was designed especially for this work in platinum thermometry by Callendar and Griffiths.

Description of the Resistance Box and Thermometers.

An accurate and detailed description of a Callendar and Griffiths box, exactly similar to the one used here, is given in Nature, Vol. 53, 1895, but a general idea of its construction may well be given here.

The arms X_1 and X_2 of the Wheatstone bridge consist of coils of equal resistance and the arms $B_1\ T_1\ T_2$ H and $B_2\ C_1\ C_2$ R H are made equal by varying the resistances in R and by moving the contact along the bridge wire. As P assumes a different temperature its resistance changes and the balance between the arms of the bridge is regained by varying R or H.

For convenience in taking temperatures in different places, long cables are used as leads to the platinum coil of the thermometer. These of course have some resistance and may also pass through varying temperatures which would give chance for error. To eliminate this, compensating leads c_1 and c_2 identical with the thermometer leads

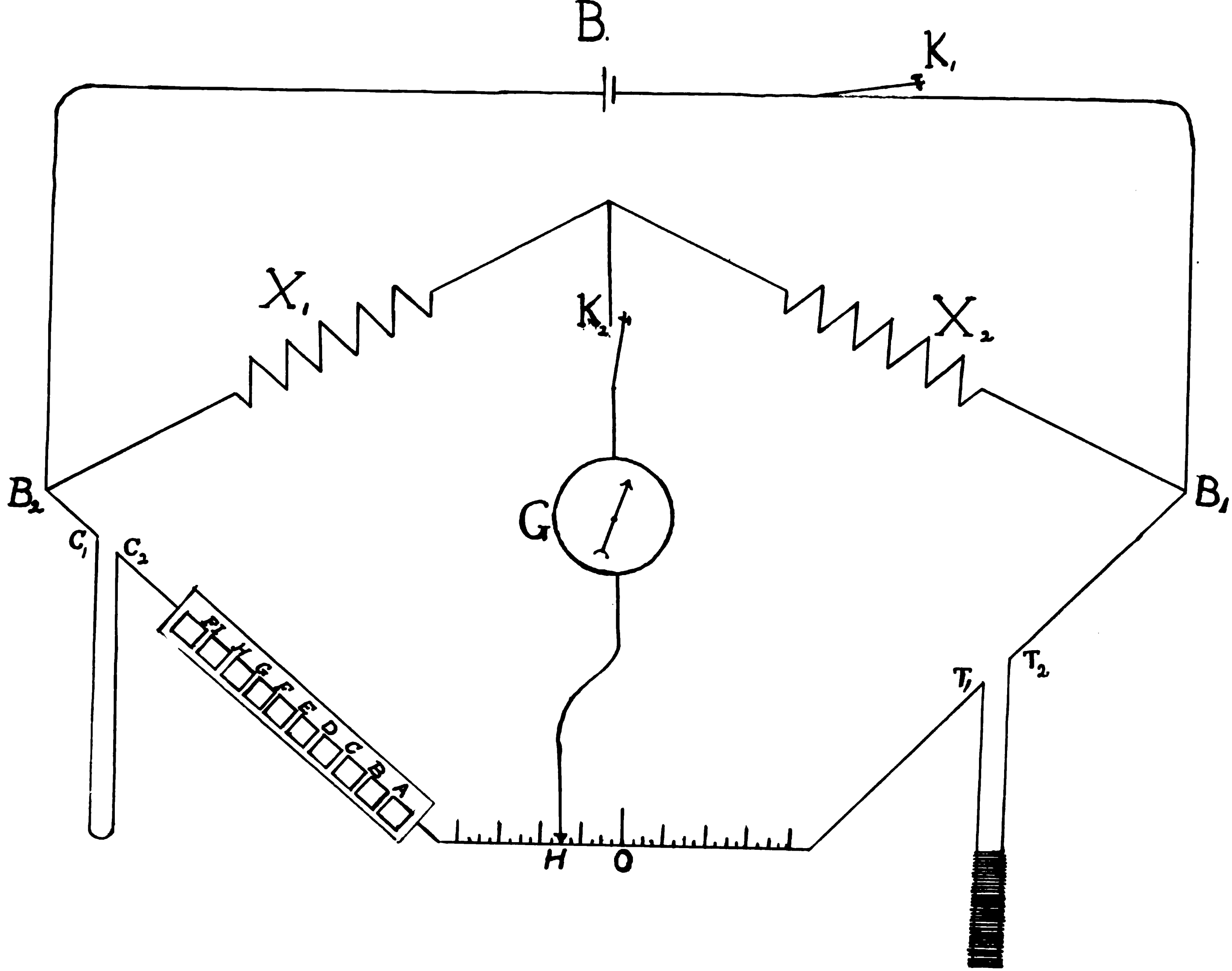

PLATE I.

are introduced into the opposite arm of the bridge. These compensating leads are wound with the thermometer leads into one cable and extend down to the coil in the thermometer so that they come in contact with exactly the same temperatures throughout, as the thermometer leads.

The coils of the box R are made of the platinum silver wire, carefully annealed and insulated. Their values are practically H=5, G=10, F=20, E=40, D=80, C=160, B=320, A=640, F=100, measured in mean box units which is 0.01 Ohm. The bridge wire of platinum silver is 30 Cm. long and has an equivalent resistance of 0.3 Ohm. The middle of the wire should be the zero, which means that if $C_1 C_2$ and $T_1 T_2$ are short circuited by thick copper wires the bridge should balance at the middle of the wire. Contact is made with the galvanometer through a similar wire stretched parallel to the bridge wire. A carefully constructed contact key* which carries a vernier reading to 1/50 mm. determines the contact. The unit division of the bridgewire is 1 Cm. and has a resistance practically equal to the mean box unit which is the unit of the coils.

With this arrangement any resistance exceeding 40 units and within the range of the bridge can be found in several ways by removing the proper plugs and adjusting

*See Nature 1895: page 42.

the contact on the bridgewire. This proves an accurate test for the bridge but is not thought to be a wise plan when taking readings of a desired temperature, owing to the fact that errors might be introduced by changing the plugs, thus changing the resistance of the contact.

The box also has two coils of 20 amd 100 ohms resistance either of which can be thrown into the battery circuit by means of a switch. This makes it possible to decrease the current should there be any thermo-electric effects produced in the bridge. A galvanometer shunt of about 1/10 the resistance of the galvanometer can also be inserted which aids very much in determining an approximate balance and also serves to protect the galvanometer against violent deflections.

A very sensitive Thompson galvanometer of 4 ohms resistance was used, which was so sensitive that it was difficult to set the contact upon a dead balance. A single Leclanche' cell, running through 100 ohms in the battery circuit furnished the current used.

For the most accurate work the coils should all be immersed in an oil bath and this surrounded by water. The water bath was omitted as it was not thought necessary for the degree of accuracy obtainable by the rest of the apparatus, and the oil bath was used only in the calibration of the coils. However, corrections were made for the

coils for every reading which were calibrated at 20°, for though the temperature coefficient of the coils was small it was found to affect the readings to 2/10ths of a degree.

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Thermometers.

The thermometers were designed by E. S. Burnett for his work as before stated,* and constructed in the Physics Department shop of the University. A description of these thermometers is necessary, as they differed considerably from any other platinum thermometer known to the writer.

The experimental method of investigation adopted by Mr. Burnett necessitated a determination of the pressure and temperature relations accompanying an irreversable expansion of fluid in the passage through a porous plug. A length of about twelve (12) feet, of three (3) inch, extra heavy pipe filled with an especially selected and graded sand constituted the plug. In order to reduce the external heat losses as much as possible, this pipe was enclosed in a 4 inch pipe and the space between maintained vacuous to prevent conduction. By way of further compensation for heat losses, the following device was adopted, A 1-1/2 inch pipe was placed coaxically within the 3 inch,

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* See thesis, E. S. Burnett, 1905.

thus dividing the plug into two parts, an inside core and a surrounding guard ring. The fluid entered either passage of the plug at the same temperature and pressure while the pressure with which it left these passages was controlled by a specially designed valve which could be adjusted to throttle the outlets independently. The object being to vary as necessary, the expansion in the two passages so that the change in the temperature might be made as nearly equal as possible, throughout each passage of the plug. It will thus be seen that within each of the three spaces, namely, the core and its surrounding passage and the guard ring there existed a different fluid pressure.

The problem was to devise a thermometer to determine the temperature of the fluid at various points as it flows through the core. In order to make it possible to remove any thermometer when desired, it was necessary to insert them radially through the three pipes. The method finally adopted is shown in plate No. II.

Considerable difficulty arose in getting a material for the core of the thermometer which would be a non-conductor of electricity and yet not be affected by the fluid The substance decided upon was red fibre which seemed to satisfy the greatest number of requirements without introducing new chances of error. The wire used for the coils

in the thermometers was of especially pure quality of platinum with a diameter of about 0.008 of an inch. This was wound in double coils about the spider-shaped fibre [*1] to a length of about 1-1/2 inches. This coil constituted the bulb of the thermometer. The two ends were then threaded through the fibre and copper leads soldered to them which terminated at four binding posts screwed into the head end of the fibre. The compensating leads were of copper, except that part of them which was in the thermometer proper and these were of platinum. Both the compensating and the thermometer leads were hermetically sealed in the fibre with a preparation of glycerine and litharge which hardens readily and is a very poor conductor of electricity. The whole thing was then enclosed in a steel case so shaped and threaded as to fit perfectly into the several pipes through which it must pass.[*2]

A long four-cable insulated copper cord connected the thermometer with the bridge, two of the cables attached directly to the thermometer leads and the other two to the compensating leads. The connection at the bridge end of the cable was made through flat copper lugs while the other end of the cable ter-

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*1 See Plate II. Fig. 3.
*2 See Plate II. Fig. 1.

minated in brass plugs that were turned to fit the hollow brass binding posts of the thermometers. This arrangement was designed to allow of a rapid change from one thermometer to another when quick readings were desired.[*1] By making this connection at the thermometer head, a single cable could be used for as many of the thermometers as was desired. It was found, however, that the contact at this junction might vary somewhat in reversing the plugs. This was considerably bettered by lengthening them, and deepening the holes in the binding posts.

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Calibration of Apparatus.

The calibration of bridge and the thermometers constituted the major part of this work. The method adopted for calibrating the bridge was in some respects similar to that used by Callendar and Griffiths and described in, Nature, Nov. 1895, but for the points of difference it is necessary to give a general outline of the whole calibration.

The corrections for the coils in R,[*2] were determined in two different ways, either one of which served conven-

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*1 See diagram of contact plug. Plate III.
*2 See Plate I. Page 8.

iently, as a check upon the other.

In the construction of the bridge the coils S_1 and S_2 were very carefully made equal as there was no ready method of testing them, and these were assumed to be correct still. The coils from A to H were determined as follows,- C_1 and C_2 were short circuited by inserting a thick copper link between its terminals, while T_1 and T_2 were connected with the terminals of a Wolff resistance box r_1. Connected in parallel with this were two other Wolff boxes r_2 and r_3. From these boxes, each of which ranged from 0.1 to 2000 ohms, almost any resistance could be found so that the bridge might be balanced with the contact at any point along the bridge wire.

On a convenient place on the bridge wire the box was balanced with all the plugs from A to H inserted. This point might be termed the zero point for these corrections. Then upon removing H the bridge was again balanced by moving the contact maker along the wire about 5 cms. to the left. By taking out the resistances in r_1 and r_2 the balance was brought back very approximately to its original position zero, and by adjusting r_3 the balance was placed exactly upon the zero point. When the bridge was again balanced at its original reading H was replaced and G removed, and the same process repeated for G that was performed on H. Each coil from A to H was tested in this

manner over practically the same 5 cms. of bridge wire and careful readings were taken of the length of wire used for each coil. This gave values for each coil in terms of H. from which corrected values for each was determined in terms of the mean box unit. The sum of all the coils was then found on the large post office box, also the value of H in the same way.

From data taken in the above way a number of equations could be written out. If Z_1 is the amount of bridge wire used when H was removed. Z_2 the amount when G. was removed Z_3 for F. and etc. then

$$A - (B \text{ to } H) = Z_8$$

$$B - (C \text{ to } H) = Z_7$$

$$C - (D \text{ to } H) = Z_6 \text{ etc.}$$

By subtracting, we get,-

$$A - 2B = Z_8 - Z_7$$

$$B - 2C = Z_7 - Z_6$$

$$C - 2D = Z_6 - Z_5 \text{ etc.}$$

From these equations, values of A, B, C, D, E, F, and G were found in terms of H. These values then subtracted from the amount each coil represented, gave the correction necessary to add or subtract in the computations used.

The second method was more accurate and simple, and consisted in finding the resistance of each coil by the direct reading potentiometer. The bridge wire was cali-

brated by the potentiometer method in much the same way and with the same apparatus as the coils were standardized. The difference of potential between the end of the wire and - 15 on the scale, was determined. This reading might be termed the zero reading in this method.

The contact was then moved to - 14 and the potential difference found, and in the same way readings for each cm. of the bridge wire were taken. From these readings the resistance of the bridge wire at each cm. was found. Then starting at the middle of the wire as zero and subtracting the resistance determined, from the amount indicated on the bridge wire scale, the correction that must be added or subtracted at each cm. was found. Several similar calibrations of the bridgewire was worked out all of which were consistent in general, though none agreed exactly.

In the calibration of the thermometers it was necessary, as was shown at the beginning of this paper, to determine the resistance at three different temperatures at least. Two of these points were temperatures generally taken in the standardizing of thermometers, namely, the freezing and boiling points of water. The third point for thermometers designed for high temperatures is usually that of boiling sulphur, but as these thermometers were designed for low temperature work, it was thought that the theoretical absolute zero would bring the parabola more nearly over the working ground. This point has been used by experimenters, and was found to hold with remarkable accuracy.

To determine the resistance at the zero point, Centigrade scale, a double walled copper vessel was used in which finely broken ice and water was placed in both compartments. The thermometers were placed in their steel cases and these firmly fixed in a plate of hard wood cut to fit the top of the inner vessel, thus eliminating any fear of radiation. With the thermometers in this position many readings were taken, and by two different observers. The observations varied considerably when readings were taken after the thermometers had been standing, but a fairly accurate and consistent set were obtained by stirring the ice about the thermometers before reading them.

The mean of a set thus determined for each thermometer was taken as the resistance for the freezing point of water.

In determining the resistance at the boiling point, a similar double vessel was used. The inner vessel contained distilled water while the outer one, a solution of salt and water. With this arrangement it was possible to boil the distilled water by applying heat to the salt solution, which gave us a steam chamber, surrounded by a steam bath. Both compartments were covered with a single wooden plate so that no steam could pass from one to the other. Two small holes were bored through the wooden plate to allow the free escape of steam from each vessel and this was conducted away from the thermometers, which were inserted into the inner one. Here again the mean of a set of readings was taken for each thermometer, as its resistance at the temperature of boiling water. By close and frequent readings of the barometer, the coil temperature of the bridge, and the time, quite accurate corrections could be applied.

The resistances at the boiling point were less consistent than that at the freezing point and many very unsatisfactory results were obtained. But with the most careful manipulations and accurate corrections and by taking the average of a large number of readings a fairly accurate set were obtained.

By way of a check upon the accuracy of the calibration of the thermometers, the resistances at the same points were determined on the large post office box with good results.

Several intermediate temperatures were determined with all the thermometers to test their accuracy and agreement.

Observations.

The observations taken are by far too voluminous to enter them all in this paper but a fair sample with the arrangement of data can well be given, together with the mean of final reading used in the standardization.

Table I. shows the readings and tabulated form of the data for the calibration of the coils of the resistance box. These were determined by the direct reading Potentiometer and are a fair sample of a great many similar readings.

Table I.

Coils.	Nominal values in Box Units Approx. .01.Ohm.	Resistance Corr. for O and Temp.	Resistance in terms of the Mean Box Unit.	Coil Corr.
H	5	5.0184	5.0143	+.014
G	10	9.9413	9.9332	-.077
F	20	20.0592	20.0428	+.043
E	40	39.9793	39.9467	-.053
D	80	79.9795	79.9672	-.032
C	160	159.7584	159.6279	-.371
B	320	320.6876	320.4257	+.426
A	640	640.1625	640.1625	-.163
F I	100	100.3728	99.9733	-.037

The above results determined by the Potential Method.

Table II. shows the results from the Calibration of the bridge wire and the correction to reduce the bridge wire to the mean box unit. A curve was plotted for the readings, and intermediate readings interpolated from the curve.

Table II.

Bridge Wire Reading.	Calibration Correction.	Bridge Wire Reading.	Calibration Correction.
+ 1	-.005	- 1	+.006
+ 2	-.012	- 2	+.008
+ 3	-.028	- 3	+.017
+ 4	-.032	- 4	+.022
+ 5	-.042	- 5	+.029
+ 6	-.044	- 6	+.036
+ 7	-.049	- 7	+.043
+ 8	-.051	- 8	+. 052
+ 9	-.059	- 9	+. 054
+10	-.066	1 10	+. 056
+11	-.068	- 11	+.065
+12	-.070	- 12	+.066
+13	-.074	- 13	+.068
+14	-.091(?)	- 14	+.057(?)
+15	-.074	- 15	+.070

Table III. represents one of the determinations of R_0 as previously described.

Table III.

Platinum Thermometer in Ice.

No.	Coils	Bridge Wire & Corr.	Temp. of Coils & Corr.	R_0
1	B D E F H = 465. Corr. + .398	+4.567 Corr. +.031 Zero +.150	21.60 Corr.+.192	470.276
2	"	-2.287 Corr. +.016 Zero. +.150	21.63 Corr.+.196	463.474
3	"	-1.841 Corr. -.013 Zero. +.150	21.65 Corr.+.198	467.575
4	"	-1.375 Corr. -.009 Zero. +.150	21.68 Corr.+.201	467.216
5	"	-6.653 Corr. -.045 Zero. +.150	21.70 Corr.+.204	472.261
6	"	-5.991 Corr. -.041 Zero. +150	21.73 Corr.+.207	471.706
7	"	-3.162 Corr.-.023 Zero. +.150	21.74 Corr.+.209	468.897
8	"	-1.466 Corr. -.011 Zero. +.150	21.75 Corr.+.210	467.214
9	"	-5.972 Corr. -.041 Zero. +.150	21.75 Corr.+.210	471.790
10	"	-2.828 Corr. -.020 Zero. +.150	21.75 Corr.+.210	468.567

Table IV. is one of the determinations made of the steam point and represents fairly the results obtained for this point.

Table IV.

Platinum Thermometers in Steam.

No.	Coils	Bridge Wire and Correction.	Temp. of Coils	Bar. Corr. For Tem	Resist. at the Obs. pr.
1	B C D E F H = 625. Corr.+.027	-2.436 Corr.-..018 Zero +.150	21.77 Corr.+.212	732.34	627.807
2	"	+4.208 Corr. +.030 Zero. +.150	21.82 +.161	732.33	621.166
3	"	-0.786 Corr. -.006 Zero. +.150	21.85 +.163	732.32	626.121
4	"	-0.572 Corr. -.004 Zero. +.150	21.89 +.167	732.31	625.913
5	"	-7.697 Corr. -.051 Zero. +.150	21.93 +.171	732.30	632.995
6	"	+6.808 Corr. -.046 Zero. +.150	21.97 +.174	732.29	632.114
7	"	+2.797 Corr. -.020 Zero. +.150	22.00 +.177	732.28	628.132
8	"	+0.254 Corr. -.002 Zero. +.150	22.07 +.183	732.27	625.613
9	"	+6.367 Corr. -.043 Zero. +.150	22.13 +.188	732.26	631.690
10	"	+2.539 Corr. -.017 Zero. +.150	22.19 +.194	732.25	627.994

Table V.

No	R_0	$\frac{R_0}{F.I}$ x 100	F. I.	δ	R_t Corr	$R_t \div R_0$	Pt	t-pt. W Form.	T cal.	t
1	470.276	-296.25	159.420	2.270	502.544	32.268	20.24	-.37	19.87	20c
2	463.474	-290.43	159.584	1.710	495.811	32.337	20.22	-.28	19.94	"
3	467.575	-291.42	160.450	1.810	500.068	32.493	20.25	-.29	19.96	"
4	467.216	-290.92	160.600	1.760	499.563	33.347	20.14	-.28	19.86	"
5	472.261	-290.89	162.663	1.760	505.286	33.025	20.30	-.28	20.02	"
6	471.706	-290.57	162.333	1.725	504.487	32.781	20.20	-.28	19.92	"
7	468.897	-290.97	161.146	1.765	501.575	32.678	20.28	-.28	20.00	"
8	467.214	-291.46	160.300	1.815	499.830	32.616	20.35	-.29	20.06	"
9	471.790	-291.55	161.819	1.820	504.607	32.817	20.28	-.29	19.99	"
0	468.567	-290.42	161.340	1.710	501.178	32.611	20.21	-.28	19.93	"

Table V. represents a test temperature taken in water at about 20° C. and also the data for determining δ which varied considerably for each thermometer. F I as shown in this table was derived from the following formula,-

$$F\ I. = R_{100} - R_0 \frac{R_s - R_0}{t_s} \times 100 - R_0$$

Where R_s = the resistance at temperature t_s of boiling water as determined by the barometer.

Concluding Remarks.

In conclusion it should be stated that the results obtained were far from what it was hoped to attain, at the outset of the work. However, the results as shown in the preceding table agree to about 1/10th of a degree which is somewhat better than could be expected of any but the very best mercury thermometers. It was hoped to measure temperature accurately to 1/100 of a degree and just how much of the failure to reach this, is due to the plug contact, or to conduction through the steel cases around each thermometer is not known at present. We are inclined to attribute the greatest source of error to the varying plug contact of the Callendar bridge, which has caused us an immense amount of trouble and must be materially improved before the work can be satisfactorily completed.

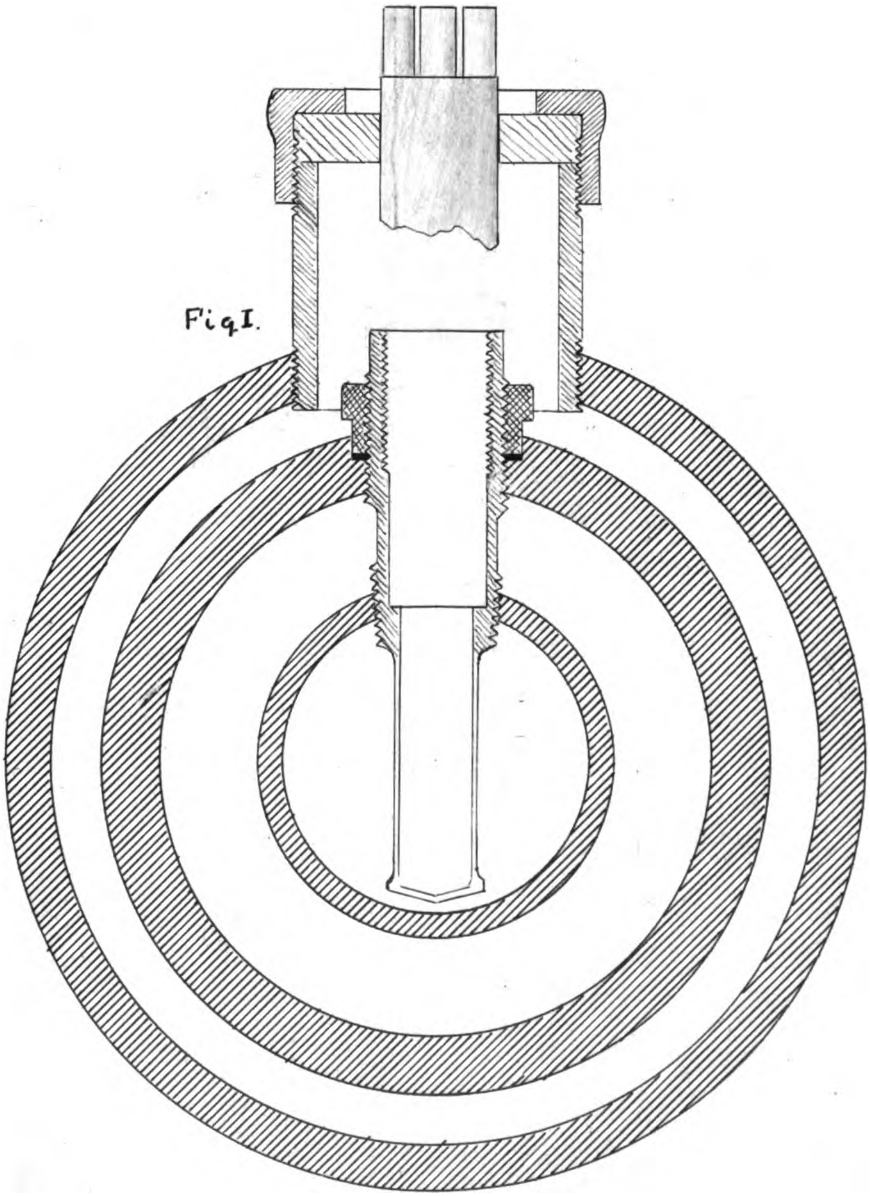

Fig I.

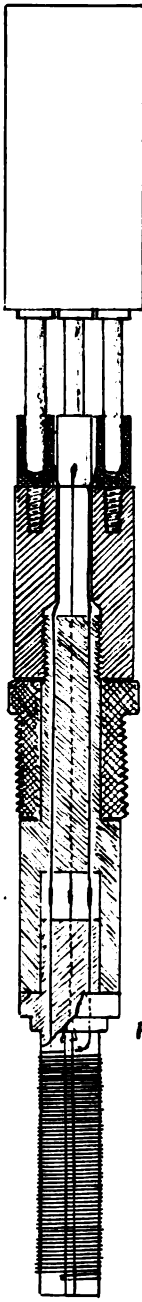

Fig. II.

Fig III.

PLATE II

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